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BULLETIN OF THE UNIVERSITY OF WISCONSIN

NO. 375

SCIENCE SERIES, VOL. 4, NO. 2, PP. 21-38.

THE SEPARATION OF THE GADOLINIUM EARTHS AS STEARATES

BY

CHARLES WARREN HILL

Instructor in Chemistry, The University of Wisconsin

A THESIS SUBMITTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
THE UNIVERSITY OF WISCONSIN
1910

MADISON, WISCONSIN
SEPTEMBER, 1910

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INTRODUCTION

The resemblance of the gadolinium earths in chemical properties to the cerium earths on one hand and to the yttrium earths on the other renders their separation doubly difficult.

On account of the mutual similarity of these earths, their isolation is one of the most unsatisfactory in rare earth work. An efficient and rapid method for the isolation of these elements is therefore of interest and importance.

The aim of the present work is the application of the separation as stearates to the earths of higher atomic weight in general and more specifically to the gadolinium earths, gadolinium, europium and samarium.

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THE SEPARATION OF THE GADOLINIUM EARTHS AS STEARATES

THE STEARATE SEPARATION

Separation of rare earth mixtures as stearates is accomplished by the addition drop by drop of a hot alcoholic solution of potassium stearate to a dilute neutral solution of the earth nitrates, in quantity sufficient for the precipitation of only a fractional portion of the earths present. The earth solution is thoroughly stirred during precipitation which begins at once with the first few drops of the stearate solution. The precipitate is curdy and lighter than water.

Better separation is effected by prolonged mechanical stirring or beating of the mixture, resulting in the formation of a fine granular precipitate which may be separated from the solution in a Büchner funnel.

The last fraction of a series is best precipitated as oxalate from the hot solution, since the excess of potassium stearate forms a slimy precipitate which it is difficult to separate from the solution.

The potassium stearate solution is prepared by dissolving 300 grams of stearic acid in a liter of alcohol, neutralizing with a solution of potassium hydroxide using phenolphthalein as indicator and diluting with water to two liters. 50 cc of such solution will precipitate a quantity of the earth stearate yielding about two grams of the oxide on ignition.

The influence of stirring was shown experimentally by precipitating fractionally a mixture of earths, the average atomic weight of which was 126. The atomic weight of the first fraction which was not stirred after precipitation was 127, while the atomic weight of the same fraction after rapid stirring for 48 hours was 135.

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SEPARATION OF RARE EARTHS FROM MONAZITE

The rare earths obtained from monazite as oxalates, ignited and converted into nitrates, were fractionally crystallized from the nitrate solution as the double magnesium nitrates, crystallization being continued until magnesium nitrate separated out. The crystallized part contained the major portion of the cerium, lanthanum and the didymiums. From the remaining solution three large fractions of insoluble double potassium sulphates were crystallized. The earths remaining in solution were treated as described on page **10.**

Insoluble Double Sulphate Portion

The earths in the last insoluble double sulphate fraction were converted into hydroxides by boiling with sodium hydroxide. The hydroxides after being washed, were dissolved in nitric acid, and the earths reprecipitated from the dilute nitrate solution by dilute ammonia, washed free from alkali, and dissolved in formic acid.

Five large fractions of formates were obtained by the slow evaporation of the formate solution, and the earths remaining in solution were precipitated by ammonia. The earths in the large first formate fraction were converted into nitrates, hydroxides, and formates successively, and fractionated partly as formates (three fractions) and as hydroxides (last four fractions). The earths in the other formate fractions were precipitated fractionally with dilute ammonia. The atomic weights determined were:

Series I

Formate Fractions	I	II	III	IV	V	VI
Subdivisions	143.5	137	134	132	138.1	119.9
	.....	.....	.....	.....	132.4	.....
	.....	.....	.....	.....	131.1	.....
	.....					
	.....					
	135.1					
	63.0					

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The last fraction of the formate fraction I, showing an atomic weight of 63, gave a white oxide and its solution showed no absorption spectrum. It consisted of yttrium and scandium.

The fractions derived from the large formate fractions I and II were separated further by fractional precipitation of the stearates. Thirty-three fractions thus obtained were combined into six groups according to the color of the oxides and their relation to the other fractions, the more soluble of one group being combined with the less soluble portion of the group following. (Series II)

The six groups were fractionated further as stearates into twenty-eight fractions, the atomic weights being determined.

SERIES III

138	146.9	144.7	150.8	144.8	146.5
			147.5		
	128.9	131.6			
113.6				124.6	

In the first part of the work, the atomic weights of only the extreme fractions were determined. This course is not advisable since the first fraction of a group is usually lower in atomic weight than the second, and often approximates an average of the group. It is to be expected with the earths under consideration, that the didymiums would be present to a greater extent in the first fractions of a series and the atomic weight of some intermediate fraction would be greatest. The atomic weights in many of the tables confirm this statement. It is therefore necessary in accurate work to determine the atomic weights of practically all the fractions of a series.

The fractions last described were combined according to the atomic weights into eight groups, the atomic weights of which approximated 148, 145, 142, 140, 137, 132, 128, 124. The first three groups, after removal of the cerium by hydrogen peroxide and ammonia, were taken for further separation as stearates. The atomic weights of the different groups and fractions are given. Each group was obtained by combination of fractions of the preceding group which had nearly the same atomic weight.

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Series IV

At. wt. of group	(148)	(145)	(142)
" " " fractions	145.8	146	148.4
	.....	.....	.....
	.....	.....	.....
	.....	121.6	.....
	131.3		137.6

Series V

At. wt. of group	(146)	(144)	(140)
" " " fractions	146.2	148	144
	147.5	139.9	143.3
	147.4		143.2
	.....		142.1
	120.1		141.3
	118.9		.....
			126

Series VI

At. wt. of group	(147.6)	(143)	(144)
" " " fractions	153.1	150.4	145.3
	146.6	150.2	143.1
	142.9	143.4	140.9
			133.7

Series VII

At. wt. of group	(153.1)	(146.6)	(143.4)
" " " fractions	152.3	151.2	149.8
	150.3	145.7	137.1
	147.8		

Series VIII

At. wt. of group	(150)	(147)
" " " fractions	149.1	149.8
	151.3	142.8

Series IX

At. wt. of group	(149.5)
" " " fractions	151.8
	153.2
	153.0
	149.8

Series X

At. wt. of group	(153)
" " " fractions	153.3
	153.0

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The fractions had now become so small that it was considered advisable to combine them with fractions of the same atomic weight and absorption spectra, which had been obtained from the soluble double sulphate portion from monazite.

Series XI showed a constant atomic weight of 153. The oxide had a light chamois color. The absorption spectrum of a ten per cent solution of the nitrate was:

Europium.	Samarium.	Erbium.
464 strong 534.5 " 592 faint	471, 478 faint 496.5, 500 haze 559 very faint	484.3, 486.8 fairly strong 543.6, 545 fairly strong 666 very faint.

The earth was europium with only the faintest traces of samarium and a small amount of erbium.

Fractions from Series VIII and IX having the atomic weight of 149.8 were found to be constant. The absorption spectrum of a 20 per cent nitrate solution was composed of strong lines of samarium, a few lines of erbium of medium strength, and one stronger one of praseodymium.

Samarium.	Erbium.	Praseodymium.
463 faint 470–475 medium 497–501.5 strong 531–535 medium.	483–485 medium 542–544.8 medium 666.6 very faint	595–604.5 strong

The earth was therefore samarium in a high degree of purity, being especially free from other members of the gadolinium group.

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SOLUBLE DOUBLE SULPHATE PORTION FROM MONAZITE

The earths remaining in solution after the removal of the insoluble double potassium sulphates as described on page 6, were precipitated as oxalates, converted into oxides and fractionated as chromates. The earths of the first insoluble chromate fraction thus obtained (at. wt. 134) were separated as chromates into four fractions having the atomic weights 141, 145, 131; 122 in order of precipitation. Cerium was present in the first fraction and was separated as ceric hydrate.

The first three fractions were fractionated as stearates, the atomic weights of the successive groups and fractions being:

SERIES A

At. wt. of group	(141)	(145)	(131)
" " " fractions	142.7 143.5 145.7 139.4	150.1 150.0 150.2 146.3 136.6	134.1 133.1 130.9

SERIES B

At. wt. of group	(143)	(146)	(150)
" " " fractions	149.6 144.4	150.8 150.2 147.9	153.2 156.0 147.8

SERIES C

At. wt. of group	(.....)	(.....)	(150.5)	(147.8)	(144.4)
" " " fractions	154. 152.8 151.5 142.5	152.2 151.9 148.9	154.0 150.4 151.8 147.7	154.7 149.9 146.0 134.5	151.0 146.1 134.6

SERIES D

At. wt. of group	(154)	(152.8)	(152.2)	(151.8)	(151.0)	(144.4)
" " " fractions	156.0 153.3	152.6 152.5	154.0 151.4	153.0 151.0	155.5 151.8	145.2 143.0

[1] Muthmann and Böhm, Berichte Vol. 36, p. 42; Vol. 33, p. 49.

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Series D contained some of the purest fractions from the insoluble double sulphate portion as well as those from series C.

The second group of the series had an atomic weight of 152.8 and yielded two fractions of atomic weight, 152.6 and 152.5. The limit of the efficiency of the stearate separation had therefore been reached for this particular earth in the quantity at hand,—about 3 grams. Spectroscopic examination revealed the presence of a very slight trace of erbium, with a larger amount of samarium, although the atomic weight was near that of pure europium, 152, and the spectrum lines of this element were strong. The lines of the absorption spectrum of a ten per cent nitrate solution were:

Europium.	Samarium.	Erbium.
485 faint	471 strong	484.3 faint
529 faint	478 strong	486.8 faint
534.4 medium	498 medium	
592.6 strong		543 faint
597 strong		548.5 faint
		666 faint

Fractions having the atomic weight of 156 and 155.5 gave an absorption spectrum of erbium and samarium (extremely faint) with practically the same lines as above with varying intensity. The gadolinium was not as pure as the europium.

Europium had therefore been obtained which contained only the slightest traces of erbium, with a very small quantity of samarium, while by the same method another sample had been obtained which contained some erbium with only the slightest traces of samarium. There can be no doubt as to the efficiency of the stearate separation although it does not appear advisable to effect the complete removal of erbium and samarium from the two samples of europium until larger portions of the earth can be obtained.

The samples of europium were obtained from the original monazite material after 59 series of fractionation yielding 204 fractions as shown below:

Double magnesium nitrates,—1 series of 3 fractions.
Double potassium sulphates,—1 series of 3 fractions.

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Insoluble Double Sulphate Portion.			Soluble Double Sulphate Portion.		
Separated as	Series.	Fractions.	Separated as	Series.	Fractions.
Formates.....	7	21	Chromates.....	1	4
Stearates.....	32	120	Stearates.....	17	53
	39	141		18	57

RARE EARTHS FROM GADOLINITE

Twenty-five pounds of gadolinite from Norway were powdered and decomposed by boiling with concentrated hydrochloric acid. Repeated boiling of the residue after decantation of the acid solution, removed nearly all of the rare earths.

The resulting acid solution was evaporated to a thick syrup which solidified on cooling. This was heated to dryness to dehydrate the silica, boiled with concentrated hydrochloric acid to decompose the basic salts formed by the heating, (largely basic ferric chloride), and extracted with water. After filtration and neutralization of the excess of the acid with ammonia, the solution was made acid with hydrochloric acid. It was found necessary in all cases of neutralization with alkalies, to work with dilute solutions of both earth and alkali, thus avoiding local precipitation and the formation of globules which enclose some of the solution and which dissolve with difficulty even when the solution is made decidedly acid. A saturated solution of oxalic acid, together with some of the crystals of acid, was added as long as precipitation resulted.

The solution was decanted, brought nearer to neutrality with ammonia and more oxalic acid added. The addition of ammonia and oxalic acid was repeated as long as was necessary for complete precipitation. After the oxalic acid had been added in excess, ammonia alone was required to bring down more of the oxalates. The first oxalates were white, but near the end of the process the precipitate was yellow or red due to iron and cerium.

The oxalates were completely washed, dried, and ignited. The mixed oxides and carbonates were dissolved by being sprinkled

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carefully into hot concentrated nitric acid. The material did not dissolve at first, but turned dark brown with the evolution of carbon dioxide, until a certain condition of either temperature or concentration was reached, when vigorous action ensued and solution was effected. Hydrochloric acid fumes as well as those of nitric acid were evolved. R. J. Meyer[4] accounts for the retention of the hydrochloric acid by the formation of oxalo-chlorides, when the oxalates are precipitated from a solution of certain acidity. A heavy dark red liquid was formed from which red crystals separated on cooling. The acid solution thus prepared was diluted to a large volume and the excess of acid nearly neutralized with caustic soda. The excess of acid cannot be removed by heating on account of the formation of basic salts. The solution at this point was yellow.

Double Sulphate Fractionation

Sixteen liters of the nitrate solution (sp. gr. 1.1554 at 17°) had been obtained in the manner described. To this solution, 200 cc of a saturated solution of sodium sulphate were added, with vigorous stirring. Precipitation resulted at once. The solution was filtered after standing twelve hours. After concentration of the solution by evaporation and cooling, two more fractions were removed by the addition of sodium sulphate solution.

300 cc of saturated potassium sulphate solution were added to the filtrate from the double sodium sulphate precipitation, and the solution evaporated until a precipitate began to form. The precipitate was pink. 200 cc of sulphate solution gave a second fraction; the fifth and sixth fractions were each precipitated by 500 cc of the sulphate solution, and each of the following fractions was precipitated by the addition of one liter of the sulphate solution until 18 fractions had been obtained and precipitation was complete. The didymiums were nearly removed in fraction 12, as shown by the color of the oxide and by the absorption spectrum of the nitrate solution. Fractions 16, 17 and 18 gave white oxides.

[4] (Abegg Handbuch III, Part I, page 148).

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Formate Fractionation

The double sulphate fractions were converted into hydroxides by boiling with concentrated sodium hydroxide solution. The hydroxides were only partially soluble in formic acid, and were therefore dissolved in nitric acid after washing to remove the greater part of the alkali, reprecipitated by dilute ammonia, and washed free from alkali, since the crystallization of the formates is influenced by the presence of alkali salts. The hydrates were dissolved in the minimum amount of formic acid (sp. gr. 1.23). The formate solution was slowly evaporated until considerable deposition had occurred. The solution was filtered and evaporated again, and the process repeated until the solution became syrupy and no more crystals could be obtained. The earths remaining in solution were precipitated by ammonia. Slow evaporation was found to be essential to the success of the process. The formates were decomposed by nitric acid and the earths precipitated as oxalates and ignited, in preference to drying and igniting the formates directly.

The eighteen double sulphate fractions had been divided into fifty-nine fractions by the crystallization of the formates. The color of the oxides, which varied from a red-brown to white, and the absorption spectrum of a 10 per cent solution of the nitrates served as a basis for the combination of these fractions into eight groups, the atomic weights of which were found later to be,—138.6, 121.1, 108, 105, 100, 102, 98.6, 99.9.

The four fractions of higher atomic weights were fractionated as double potassium sulphates, the atomic weights being:

At. wt. of group	(138.6)	(121)	(108)	(105)
At. wt. of fractions	135	136	120.2	118.3
	.....	.....	107.8	107.4
	133	.....	105	101

These fractions were combined according to atomic weight and the three heavier groups, after removal of cerium, were fractionated as stearates. The atomic weights were:

At. wt. of group	(136)	(135)	(133)
At. wt. of fractions	138.2	136.1	140.9
	135	135.6	134.5
	127.2	124.8	.....

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The heavier fractions contained only a small amount of the gadolinium earths desired in our work,—erbium, samarium, showing faint lines in the spectrum. Lanthanum and the didymiums constituted the major portion of these fractions. The gadolinite was richest in yttrium and contained but little of the earths of higher atomic weight. Work with these earths was therefore abandoned, and the gadolinium earths extracted and separated from monazite as described.

The material from gadolinite had been subjected to 27 series of separations yielding 109 fractions,

Double sodium sulphate separation	1	series	of	4	fractions
" potassium sulphate "	1	"	"	18	"
Formate separation	18	"	"	59	"
Double potassium sulphate separation	4	"	"	12	"
Stearate separation	3	"	"	6	"
	27	"	"	109	"

THE STEARATE SEPARATION OF THE CERIUM EARTHS

The efficiency of the stearate separation when applied to the earths of the cerium group is shown by series V (page 8) where groups of the atomic weights 140, 144, and 146 were fractionated, also by series VI, and certain groups in series VII, and IX, in the insoluble sulphate portion. Series A, B, C, D (page 10) in the soluble sulphate portion show the same efficiency.

Spectroscopic examination of the groups and fractions indicated a partial separation of the didymiums, while cerium was concentrated in the first few fractions as shown by the hydrogen peroxide and ammonia test.

While none of the members of this group were isolated, the separations effected in this group while seeking the members of the gadolium group leave no doubt as to the efficiency of the stearate separation in the cerium group.

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ATOMIC WEIGHT DETERMINATION[5]

For the determination of the atomic weights, about one gram of the oxide was weighed out roughly, sprinkled into 3 or 4 cc of concentrated nitric acid and heated. The solution thus effected was evaporated to a thick syrup which dissolved in water. When working with fractions rich in cerium earths, a basic salt separated out on dilution and heating, in which cases it was necessary to use more acid and to avoid heating as much as possible.

The acid solution was diluted to 800 cc and heated to boiling, and a cold saturated solution of pure oxalic acid added drop by drop. The solution was thoroughly stirred during precipitation, allowed to stand a minute, when the supernatent liquid was tested with a few drops of oxalic acid solution. The oxalate settled rapidly if the solution had been heated sufficiently before precipitation. The solution was allowed to stand over night, when the liquid was decanted on to a filter and the oxalate washed five times with boiling water by decantation, thrown onto the paper and there washed five times. The oxalate was dried at 110°–120°.

The dry oxalate was thoroughly pulverized in an agate mortar, and two portions of about 0.2 grams weighed out, one for the determination of the oxide ratio and the other for the acid ratio. One portion was ignited in a platinum crucible to constant weight. The percentage of R_2O_3 was thus determined. The other portion was suspended in 100 cc of water, and solution effected by addition of 8 cc of concentrated sulphuric acid. The solution was diluted to 400 cc, heated to about 80° and the oxalic acid liberated was titrated with a standard potassium permanganate solution. The percentage of C_2O_3 was thus determined. From the two determinations, the atomic weight of the earth was calculated.

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[5] Urbain, Bul. Soc. Chim. de France 1909 page 133.
R. J. Meyer (Abegg Handbuch Vol. III, 1 page 172).
Baxter and Daudt, Journ. Amer. Chem. Soc. Vol. XXX, page 563.

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SUMMARY OF EXPERIMENTAL WORK

After division by potassium double sulphate, the rare earths from monazite were fractionated as stearates, until the gadolinium earths were concentrated and separated. Eighteen series of 57 fractions from the soluble double sulphate portion yielded a fraction of constant atomic weight of 152.5, which was practically pure europium. A second sample of europium (atomic weight 153), containing a trace of erbium, was separated from the insoluble double sulphate portion by 39 series of 141 fractions. The separation at the same time yielded a sample of impure gadolinium of atomic weight of 156, which contained some erbium, samarium, and europium, and also a sample of samarium of atomic weight 149.8.

The rare earths were extracted from twenty-five pounds of gadolinite and fractionated by 31 series of 129 fractions. The mineral contained quantities of the gadolinium earths too small to warrant their separation.

In the entire work 90 series of fractionations yielded 333 fractions of which 159 were analyzed and the atomic weight of the earth determined.

CONCLUSIONS

The experimental work described demonstrates that:

1. The gadolinium earths may be concentrated and separated by their fractional precipitation as stearates.

2. The stearate method is also applicable to the separation of the members of the cerium group.

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